25
ENERGY IN LIQUID STATE

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ABSTRACT. Potential energy is calculated for water between 30°C and 365°C, assuming the surface of the liquid to be a potential barrier for the passage of a molecule from the liquid to the vapour state. The changes in the free energy and the internal energy and the rate of variation of the former with temperature are calculated for the same range of temperature. Similar values are suggested for other liquids but at their critical temperatures only.

This paper is a continuation of a previous one by the author (Soonawala, 1936). Reviewing that paper in brief, the probability of transition of a molecule from the liquid to the vapour state was calculated assuming the surface to be a potential barrier. As the potentials of the liquid, the surface, and the vapour were there selected, it amounted to taking $W-U_0$ and $W-U_2$ in Eqn(2) of the original paper to be the kinetic energy of the molecule, and $W-U_1$ to be equal to the kinetic energy less $2mL$, where m is the mass of the molecule and L the latent heat of transition (Frenkel). This was in accordance with Laplace's theory of capillarity, which assumes $2L$ to be the work necessary to remove a unit mass of the liquid and scatter it as gas at the temperature of transition so that the molecules are so widely separated that no interaction exists between them. If n is the number of molecules per c.c. in the liquid, the number per c.c. in the vapour would be given by nF, where F is the calculated probability of passage of a liquid molecule across the barrier into the vapour state. Thus, F would be the ratio of the densities of the saturated vapour and its liquid, provided the molecules in the vapour state are so widely separated that there is no interaction between them. This would hold for low vapour densities such as are obtained at the lower temperatures. If $b/2$ is the potential energy per unit mass of the liquid, the probability F was found to be of the form $AI.\ \exp(-kmb)$, where A is a function of the mass of the molecule and the temperature, k is the Boltzmann constant, and I an integral depending upon k, m, and b. (Eqns. (8), (12) and (13) of the original paper). It was found that F so calculated did not agree with the ratio of the densities when b was assumed to be equal to $4L$, as required by Laplace's theory of capillarity. Thus, at the critical temperature, $L=0$, and $b=0$, and $F=9.5\times10^8$, while the ratio of the densities must necessarily be equal to one. This led to the conclusion that b was not equal to zero but had a value, β, such that F became equal to one. This reduces to multiplying $AI.\ exp\ (-kmb)$ by a factor, $exp\ (km\beta)$. This gives the potential energy of the liquid at the critical temperature as β_2. This is taken as a clue that a similar procedure is necessary for bringing the values of F in line with those of r, the ratio of the densities of the saturated vapour and its liquid at other temperatures also by multiplying or dividing, as the case may be, by a factor, $exp.\ (km\ \beta)$. Thus, as seen from

equations (13) and (22) of the previous paper, β becomes an addition to be, and the potential energy of the liquid becomes equal to $\frac{1}{2}(b+\beta)$. These calculations are here carried out for the temperatures 30°, 70°, 100°, 180°, and the critical temperature, 365°C, and the results are summarized in Table I. The first and second rows give the latent heat per gram in calories and ergs, respectively. The values of F are shown in the third row, and those of r in the fourth row, β is calculated in the sixth row from the relation $exp.\ (km\beta) = r/F$, or F/r, according as r is greater or less than F. This gives

$$A.I.\ exp\ (-km(b+\beta)) = r\ ;$$

from which

$$\beta = 1/km.\ ln.A/r + 1/km.\ lnI - b.$$

If b is changed by an amount c to $b+c$, β changes to $\beta + c'$, so that

$$\beta + c' = 1/km.\ ln.A/r + 1/km.\ lnI_1 - b - c,$$

where I' corresponds to $b+c$. This gives

$$c' = -c + 1/km.\ lnI'/I.$$

As I depends principally upon km and to a lesser extent upon b, we find c and $-c'$ almost equal in value. Thus, $b+\beta$ adjust itself to a constant value inspite of any errors in the assumed value of b. The fifth row shows the values of b taken to be equal to 4Q, and the calculated values of β are included in the sixth row. The sign assigned to β is with reference to b taken positive.* The seventh row shows values of $\frac{1}{2}(b+\beta)$, which is the potential energy per unit mass of the liquid. This is seen to increase steadily with temperature, as it should when referred to a ground state where the molecules are bound together as firmly as possible. The increase with temperature is due to the loosening of the bond which holds the molecules together under a force of attraction. Thus, $\frac{1}{2}(b+\beta)$ measures the work done per unit mass in loosening the bonds between the molecules from a state of firm compression to the mean molecular distance proper at the temperature concerned, transporting the molecules in the unit mass across the surface of the liquid, and scattering them as free gas at that temperature. This will, therefore, correspond to the change in the free energy, H, between the states of firm compression of the molecules and their infinite separation as a gas. We can also calculate the corresponding change in the internal energy, E. This will be given by $dQ = p.dv$, where dQ is change in the heat content of the system, and p.dv measures the work of external expansion. In the first stage of the transition, when the molecular bonds are loosened in the liquid, there is no heat absorption nor any work of expansion against external pressure, all the work being done against the large internal pressure. An amount of heat, equal to the latent heat, is absorbed during the second stage of passage from the liquid to the vapour state, and an amount of external work, equal to $p(v_2 - v_1)$, is also performed, p being the pressure during the transition

* All values of β and ϕ given in Table II of the original paper have to be multiplied by a factor of 5·30, as, due to an oversight, the factor 0·4343 was used instead of 2·303 in transforming from hyperbolic to ordinary logarithms.

and v_1 and v_2 the specific volumes of the liquid and the vapour, respectively. We expect the Thomson equation, $H = E + T.\ dH/dT$ to hold. The values of $H - E$, or, $H - Q + p\ (v_2 - v_1)$ are given in the ninth row, and those of the quotient of this quantity and the absolute temperature in the tenth row, which thus shows the values of dH/dT. The figures indicate a slow increase of dH/dT with temperature. On the other hand Fig. 1. illustrates the variation of H with temperature as given by the data of the seventh row. The value for the critical temperature is not included, as, due the increase in density, we cannot treat the state as one of infinite separation of the molecules. The figure shows a value of dH/dT equal to $7{\cdot}3 \times 10^7$ ergs per degree centigrade between 30°C and 180°C, which agrees well with the figures in the tenth row, ranging from $6{\cdot}5 \times 10^7$ to $7{\cdot}7 \times 10^7$. This completes the treatment for water of the calculations of variations of the internal energy, free energy and its rate of change with temperature between 30°C and the critical temperature, 365°C.

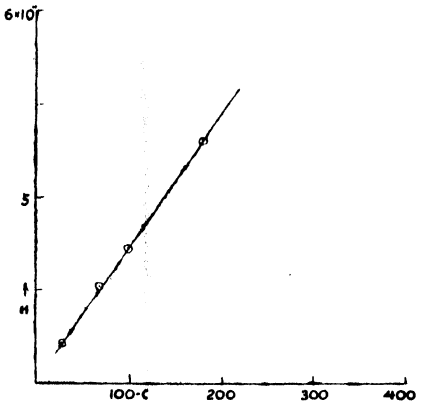

Fig. 1

It is not possible to carry out similar calculations for other liquids as the relevant data about the densities of the liquids and their vapours are lacking. Making certain comparisons between the behaviour of the integral I for water and several such liquids, the values of β were calculated for a number of liquids at the critical temperatures, as shown in Table II of the original paper. $\beta/2T$ would give the approximate values of dH/dT, but only at the critical temperature in each case ; and then also the limitations mentioned above have to be borne in mind.

TABLE 1

	30°C	70°C	100°C	180°C	365°C	
L ..	580·3	557·9	539·0	482·2	0	cals.
Q LJ ..	2·426	2·332	2·253	2·015	$9{\cdot}0 \times 10^{10}$	ergs.
F ..	$2{\cdot}75 \times 10^{-4}$	$8{\cdot}0 \times 10^{-5}$	$2{\cdot}05 \times 10^{-3}$	3·00	$9{\cdot}5 \times 10^{8}$	
r ..	$2{\cdot}64 \times 10^{-5}$	$1{\cdot}98 \times 10^{-4}$	$6{\cdot}32 \times 10^{-4}$	$5{\cdot}9 \times 10^{-3}$	1	
b 4Q ..	9·70	9·33	9·01	8·06	$0{\cdot} \times 10^{10}$	ergs.
β ..	$-1{\cdot}26 \times 10^{10}$	$2{\cdot}84 \times 10^{9}$	$+4{\cdot}01 \times 10^{9}$	$+2{\cdot}56 \times 10^{10}$	$+1{\cdot}21 \times 10^{11}$	ergs.
$H = \frac{1}{2}(b+\beta)$	4·22	4·52	4·71	5·32	$6{\cdot}01 \times 10^{10}$	ergs.
$p(v_2 - v_1)$	1·61	1·61	1·71	1·91	$0{\cdot} \times 10^{9}$	ergs.
H—E ..	1·96	2·35	2·63	3·50	$6{\cdot}01 \times 10^{10}$	ergs.
$\frac{H-E}{T}$ ..	6·5	6·9	7·0	7·7	$9{\cdot}44 \times 10^{7}$	

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